STRUCTURE AND PROPERTIES OF CeRhSn — A VALENCE FLUCTUATING SYSTEM*

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X ray diffraction studies have been performed on a CeRhSn single crystal and its anomalous unit-cell volume was confirmed. This, together with temperature dependence of magnetic susceptibility indicate valence-fluctuating behaviour of Ce ions. Band structure calculations support such a behaviour. Anomalous value of the quadrupole interaction constant derived from ^{119}Sn Mössbauer spectroscopy is observed. Ac and dc magnetic susceptibility investigations as well as preliminary resistivity measurements evidence that this compound does not order magnetically down to 2 K, but one of our samples is superconducting with a transition temperature of 6.5 K.

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1. Introduction

Cerium based ternary compounds CeTX (T transition metal, X p-element) show many interesting physical properties such as the Kondo effect, valence fluctuations, heavy fermion behaviour or different types of magnetic order-

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ing, which depend on the degree of the hybridisation between $4f$ electrons with the conduction electrons [1–4]. For example, CeRhSb and CeRhAs were found to be Kondo semiconductors [1, 2] and simultaneously the first compound has a mixed valence character. Valence instability was also discovered for CeRhP [2] and CeRhIn [3].

The title compound was first reported by Routsi *et al.*, [5], however, their lattice parameters are not correct and magnetic susceptibility measurements shown up to 120 K led only to a conclusion that Curie–Weiss behaviour is not observed. Recent measurements showed that lattice parameters of CeRhSn differ significantly from the plot of the cell volumes for the whole series of RERhSn stannides [6] and a deviation of the cerium compound from the usual lanthanide contraction is clearly observed.

In this work new X ray investigations carried out on a CeRhSn single crystal are presented together with the results of ac and dc magnetic susceptibility and ^{119}Sn Mössbauer spectroscopy measurements performed in the temperature range from 2 K to 300 K on a polycrystalline sample.

2. Experimental results and discussion

CeRhSn was prepared by reaction of the elements in a sealed tantalum tube in a high-frequency furnace. The structure was refined from single crystal X ray diffraction data: ZrNiAl type, space group $P\bar{6}2m$, $a = 745.8(1)$, $c = 408.62(9)$ pm, $wR2 = 0.0379$, for 354 F^2 values and 14 variable parameters. Refinement of the occupancy parameters revealed full occupancy of all four atomic positions within one standard deviation. No deviation from the ideal composition is observed.

The present single crystal study [6] confirmed the values of the lattice parameters derived in our recent investigations [7] on powder samples, revealing that they are indeed different from those given by Routsi *et al.*, [5]. The course of the cell volumes now unambiguously indicates the mixed valent behaviour of the cerium atoms. The CeRhSn structure contains two crystallographically different rhodium sites which both have a tricapped trigonal prismatic coordination: [Rh1Sn$_3$Ce$_6$] and [Rh2Sn$_6$Ce$_3$]. Together the rhodium and tin atoms build a three-dimensional polyanion in which the cerium atoms fill distorted hexagonal channels.

The Mössbauer spectroscopic investigations employing the ^{119}Sn 23.875 keV transition were carried out in the temperature range 2 to 300 K. In accordance with the non-cubic symmetry ($m2m$) of the tin sites, all recorded spectra show only pure quadrupole splitting, and can be easily fitted with a single component confirming high purity and homogeneity of our sample. The isomer shift $\delta_{is}(4.2\,K) = 1.82(1)$ mm/s (in respect to Ba^{119}SnO$_3$ source) is in the limit of error equal to the value obtained at room tem-

perature $\delta_{is}(293\,K) = 1.81(1)$ mm/s being typical and comparable to the values measured in other RERhSn stannides and most generally tin intermetallics [7] (and references therein). The quadrupole interaction constant $\Delta E_Q = eQV_{zz}(2.1\,K) = 1.10(1)$ mm/s does not change remarkably as a function of temperature but is clearly higher than observed in other members of the RERhSn family [7] indicating an anomalous character for CeRhSn. This resembles the situation found for the antiferromagnetic heavy fermion stannide CeAgSn against a background of the REAgSn series [4].

Fig. 1 shows the temperature dependence of the inverse dc magnetic susceptibility measured by means of SQUID magnetometer, in an applied field of 1 kOe. No phase transition of magnetic origin was detected down to 2 K. Above 120 K the temperature dependence of the magnetic susceptibility can be described by a modified Curie–Weiss law in the form: $\chi = \chi_0 + C/(T - \Theta_p)$ where χ_0 is the temperature independent term. The least squares refinement

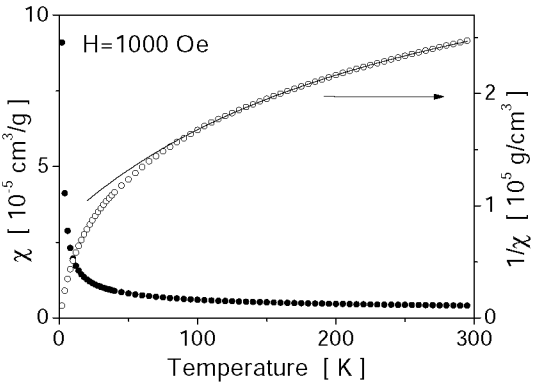

Fig. 1. Magnetic dc-susceptibility of CeRhSn in $H = 1000$ Oe. The solid line is the Curie–Weiss fit in the temperature range 120–300 K (see text).

results in $\mu_{eff} = 1.30\mu_B$/Ce ion, highly negative $\Theta_p = -70$ K evidencing antiferromagnetic correlations, and relatively big $\chi_0 = 0.87 \times 10^{-3}$ emu/mole which is comparable to the values obtained for valence fluctuating CeRhP (1.30×10^{-3} emu/mole) [2] or CeRhIn (1.13×10^{-3} emu/mole) [3]. The derived effective magnetic moment is significantly reduced in comparison with the theoretical value for a free Ce^{3+} ion $\mu_{eff}^{th} = 2.54\mu_B$, giving another hint for an intermediate valence behaviour of cerium. Since the magnetic moment of tetravalent cerium is zero, so then the observed reduction of the magnetic moment could be explained in a natural way by fractional occupation of $4f^0$ (Ce^{4+}) and $4f^1$ (Ce^{3+}) states. In this context the Sales and Wohlleben (SW) phenomenological ICF-model [8] was considered. However, it was found out that such a model does not fit properly our susceptibility data. The reason is that for a negative excitation energy E_x, the SW

formula [8] gives only a small reduction of the effective magnetic moment of cerium at high temperature *i.e.* $\mu_{\text{eff}} = \sqrt{6/7}\,2.54\mu_{\text{B}} = 2.35\mu_{\text{B}}$ while for positive E_x the resulting $\chi(T)$ function has a broad maximum which is not observed experimentally. The observed reduction of the effective magnetic moment is too strong to be explained by crystalline field effects.

Electronic band structure calculations, carried out using the TB-LMTO [9] and WIEN2k [10] program packages, confirm the metallic character of CeRhSn. Spin polarized calculations resulted in no magnetically ordered ground state for the Ce $4f$ shell. Even forcing the magnetic Ce^{3+} configuration using the fixed-spin method showed no energy gain compared with the nonmagnetic Ce^{4+}. Thus both states appear to be energetically equivalent, which reflects the valence fluctuating behaviour of CeRhSn. The chemical bonding analysis shows strong Rh–Sn bonding within the $[RhSn]^{\delta-}$ polyanion.

Below $T_{\text{C}} = 6.5\,\text{K}$ one of two our samples undergoes a superconducting transition as documented in Fig. 2 by a sudden diamagnetic drop of the dc susceptibility measured in a magnetic field of 3.6 Oe after cooling the sample in zero magnetic field (ZFC). At the same temperature a fall of resistivity is observed. The resistivity does not decrease to zero, but it may be a result of weak superconducting links between superconducting grains, since the measurement was done using a pellet obtained by pressing powder material.

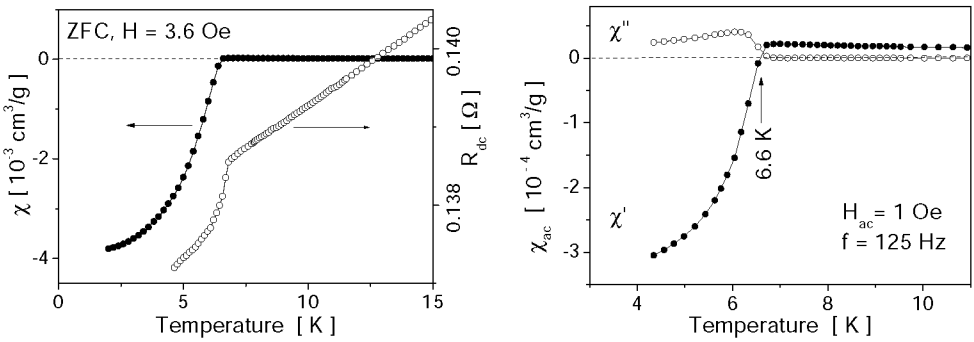

Fig. 2. Left: dc-susceptibility of our CeRhSn sample measured in $H = 3.6\,\text{Oe}$ after zero field cooling. Resistivity measured on the pressed powder pellet is also shown. Right: real χ' and imaginary χ'' parts of the zero field ac magnetic susceptibility for CeRhSn.

The transition into the superconducting state is also confirmed by the characteristic hysteresis loop below T_{C} (not shown) as well as by the onset of the diamagnetic signal in χ' at $\text{T} = 6.6\,\text{K}$ associated with the maximum of χ'' (Fig. 2) and the distinct maximum of the third harmonic (not displayed

here) observed close to the transition temperature. The superconducting fraction was estimated from magnetic measurements (without taking into account the demagnetization factor) to be about 10%.

3. Conclusions

X-rays, ac and dc magnetic susceptibility measurements, support anomalous behaviour of CeRhSn associated with valence fluctuation. It was shown that the Sales–Wohlleben ICF model is not adequate to describe the temperature dependence of the magnetic susceptibility. A superconducting transition was detected for one CeRhSn sample but further investigations are needed to recognise the origin of this superconducting state.

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